QUANTA CHEMISTRY

An Institute of Chemical Sciences

DPP- 01 Group Theory

1. According to rules of symmetry there is only one principal axis and many subsidiary axis present in a molecule, the principal axis is one which is

   (a) Parallel to Horizontal Plane

   (b) Perpendicular to vertical plane

   (c) Perpendicular to Horizontal Plane and is of lowest order

   (d) Perpendicular to Horizontal Plane and is of Highest order

2. The symmetry group is C_2 for the molecule/ion

   (a) H_2O (b) H_2O_2 (c) SO_2 (d) NO_2^-

3. Total number of symmetry elements present in HCl molecule

   (a) 3 (b) ∞ (c) 4 (d) 2

4. How many C_2 are present in S_4N_4?

   (a) 1 (b) 2 (c) 3 (d) 4

5. The symmetry element, not belong to NH_3 molecule.

   1. Inversion 2. C_2 3. C_3 (d) C_4

   (a) 1 only (b) 1 and 2 only

   (c) 1, 2 and 4 (d) 1 and 4 only

6. The principal axis present in norbornane is:

   (a) C_2 (b) C_3 (c) C_6 (d) C_∞

7. Conversion of boron trifluoride to tetrafluoroborate accompanies:

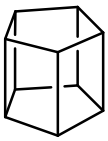
   (a) Increase in symmetry and bond elongation.

   (b) Increase in symmetry and bond contraction

   (c) Decrease in symmetry and bond contraction

   (d) Decrease in symmetry and bond elongation.

8. Which of the following symmetry element does not present in the following object.



Eclipsed pentagons

(a) C_5 (b) $5C_2 \perp C_5$ (c) S_5 (d) i

9. Which of the following statement is incorrect regard a chiral molecule.

(a) It has superimposable mirror image (b) lack of centre of symmetry

(c) lack of alternate axis of symmetry (d) All of the above

10. For an octahedron, number of C_3 axis is

(a) 0 (b) 3 (c) 4 (d) 8

11. Which of the following does not contain a C_3 axis?

(a) $POCl_3$ (b) $[NH_4]^+$ (c) $[H_3O]^+$ (d) ClF_3

12. Which of the following species posses both C_3 and C_2 axis?

(a) SO_3 (b) NH_3 (c) PCl_3 (d) $[H_3O]^+$

13. Which of the following molecule or ions possesses a C_4 principal axis?

(a) XeF_4 (b) CF_4 (c) SF_4 (d) $(PF_4)^+$

14. What is the principle axis in H_2O molecule

(a) C_2 (b) C_3 (c) C_4 (d) None of these

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ANSWERS

1. d
2. b
3. b
4. c
5. c
6. a
7. a
8. d
9. a
10. c
11. d
12. a
13. a
14. a

HINT & SOLUTIONS

1. (d)

Sol.The principal axis is one which is perpendicular to horizontal plane and is of highest order.

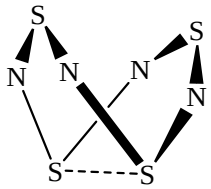
2. (b)

Sol. H_2O_2 have the open book structure, it contain only C_2-axis as symmetry operation.  have C_2—symmetry point group.

3. (b)

Sol.Point group of HCl is $C_{\infty v}$, and have $C_{\infty}, \infty\sigma_v, E$ i.e. ∞ symmetry elements.

4. (c)

Sol. 

It has C_2 as principal axis and $2C_2$ perpendicular to the principal axis and have σ_d so "D_{2d}" is the point group.

5. (c)

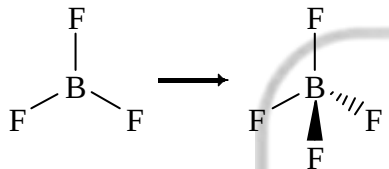
Sol.NH_3 molecule have C_{3n} point group it contains E, C_3 and σ_v, it do not contain i, C_2, C_4.

6. (a)

Sol. 

C_2 (Principal axis)

7. (a)

Sol. 

(planar) (Td)

Converting from planar to tetrahedral intend to increased the symmetry and due to decrease in the %s character there is bond elongation

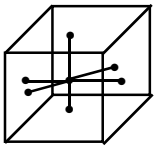
8. (d)

Sol.This object contains C_5 axis as a principal axis, 5 perpendicular C_2 axis to C_5, and improper rotation axis (S_5) but does not have COS.

9. (a)

Sol. A chiral molecule must not have any alternate axis of symmetry, centre of symmetry and plane of symmetry, and it has mirror image to which it is non superimposable.

10. (c)

Sol. 

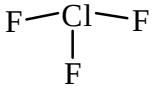
Fitting octahedral in cube.

It has C_3 axis passing through body diagonal of cube three are 4 body diagonal.

So, number of C_3 is "4".

11. (d)

Sol.ClF_3 does not C_3 axis

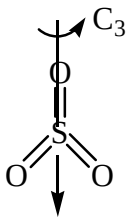


Bent T-shape

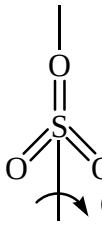
rest all have C_3 axis of symmetry.

12. (a)

Sol.



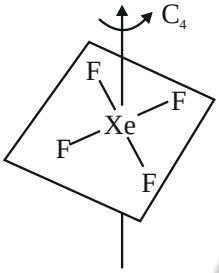
(perpendicular to plane of SO_3)



(in plane of SO_3)

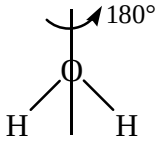
13.(a)

Sol.



14.(a)

Sol.



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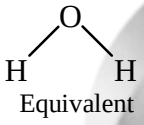

Equivalent

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QUANTA CHEMISTRY

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DPP- 02 Group Theory

1. Molecule which contain centre of symmetry

   (a) Ethene (b) HCl (c) NH_3 (d) SF_4

2. Molecule which contain centre of symmetry

   (a) Ethene (b) XeF_4 (c) XeF_2 (d) All of these

3. The number of C_2 axes is SF_6 are,

   (a) 6 (b) 3 (c) 9 (d) 12

4. Which of the following matched incorrectly?

Symmetry	Maximum no. that any molecule poses
(a) S_2	1
(b) i	1
(c) σ_h	1
(d) C_2	infinite

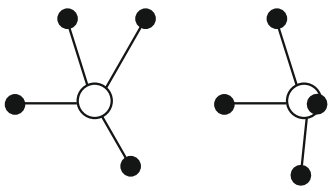
5. Which of the following molecule or ions poses an inversion centre?

   (a) $[PF_6]^-$ (b) SiH_4 (c) BF_3 (d) PF_5

6. What symmeetry elements are lost in going from NH_3 to NH_2Cl

   (a) C_3 only (b) two σ_v (c) Both (a) and (b) (d) Neither (a) nor (b)

7. Below is a molecule of AX_4 with different view. What is possible axis of symmetry for this molecule?



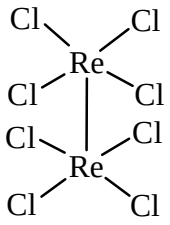
   (a) C_4 (b) C_2 (c) C_3 (d) None of these

8. BH_3 and NH_3 posses trigonal planar and trigonal pyramidal structure respectively what symmetry element possessed by both molecules

(a) Centre of symmetry (b) Vertical sigma plane

(c) Horizontal sigma plane (d) S_3 improper rotation

9. Complex of $[Re_2Cl_8]^{2-}$ is shown below. Predict how many C_2 rotation is allowed



(a) 2 (b) 3 (c) 4 (d) 5

10. Predict which molecule contains S_4 without C_4 axis?

(a) PBr_3 (Trigonal pyramidal) (b) ICl_4^- (square planar)

(c) SO_4^{2-} (tetrahedral) (d) $1Cl_2Br_2$(square planar)

11. What is principal axis in triangle

(a) C_2 (b) C_3 (c) C_4 (d) None of these

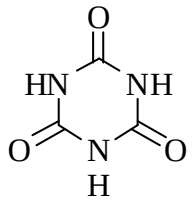
12. What is principle axis in square

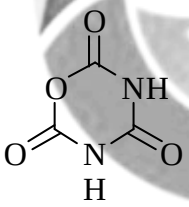
(a) C_2 (b) C_3 (c) C_4 (d) None of these

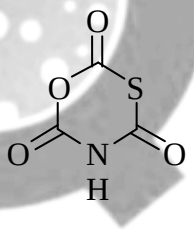
13. What is the principal axis in $POCl_3$?

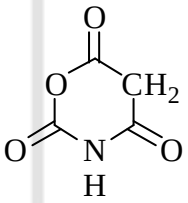
(a) C_5 (b) C_4 (c) C_5 (d) C_2

14. Out of the following molecules which one contains maximum symmetry operations

(a) 

(b) 

(c) 

(d) 

15. Which of the following is correct?

(a) $C_2^z \times \sigma_{xz} = E$ (b) $C_2^z \times \sigma_{xz} = C_2^z$ (c) $C_2^z \times \sigma_{yz} = \sigma_{yz}$ (d) $C_2^z \times \sigma_{xz} = \sigma_{yz}$

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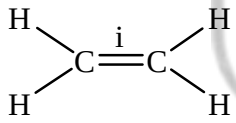
ANSWERS

1. (a)
2. (d)
3. (c)
4. (c)
5. (a)
6. (c)
7. (b)
8. (b)
9. (d)
10. (c)
12. (c)
14. (a)
15. (d)

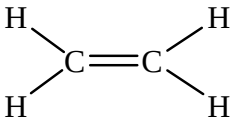
HINT & SOLUTIONS

1. Ethene

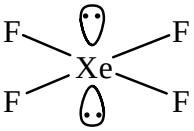


this molecule contain inversion centre, have pair of molecule on opposite sides.

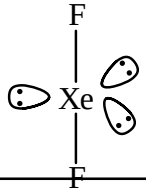
2. Ethene



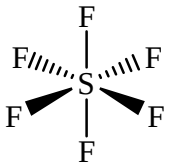
XeF_4



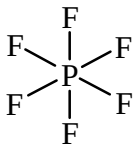
XeF_2

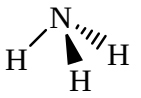


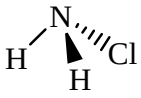
clearly all of these contains inversion centre (d)

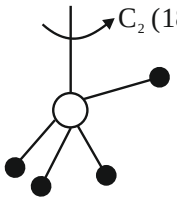
3.  (Octahedral)

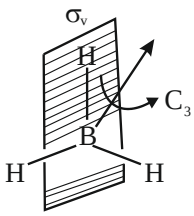
A molecule can have infinite number of C_2 (linear molecule) but have only one S_2, inversion centre (i) and σ_h can be 1 or more than 1 (in case of Octahedral). So, correct answer is (c).

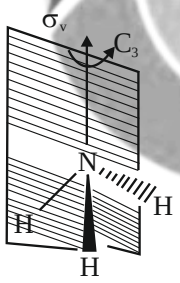
5.  Oh has S_2 or '*i*'

6.  $C_{3v} = E, C_3, 3\sigma_v$

 $C_s = E, \sigma_v$

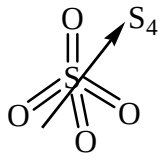
7. 

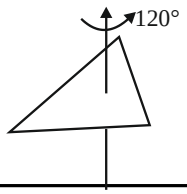
8. 



9. $4C_2$ passing through the centre of Re – Re bond and 1 C_2 through Re – Re bond, so total three are $4 + 1 = 5$ C_2 rotation allowed.

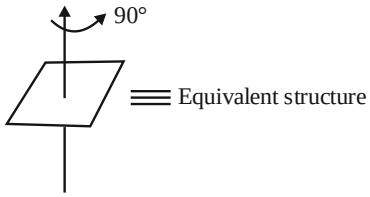
10. In a tetrahedral geometry, there is C_3 axis is principal axis but number C_4 axis is not present in tetrahedral; but it has S_4 axis passing through adjacent triangular faces.

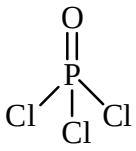


11. 

give equivalent structure,

Hence, C_3 is principle axis.

12. 

13. 

has C_3 (principal axis) and have σ_v point group C_{3v}.

14. 'a' is the correct option, because it have point group D_{3h} and having 12-symmetry operations, which are maximum in number.

15. $C_{2z}\sigma_{xz} = \sigma_{yz} \neq E$

$C_{2z}\sigma_{xz} = \sigma_{yz} \neq C_{2z}$

$C_{2z}\sigma_{yz} = \sigma_{xz} \neq \sigma_{yz}$

$C_{2z}\sigma_{xz} = \sigma_{yz} = \sigma_{yz}$

So, 'd' is correct option

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QUANTA CHEMISTRY

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DPP-(3) GROUP THEORY

1. According to rules of symmetry there is only one principal axis and many subsidiary axis present in a molecule, the principal axis is one which is
   (a) Parallel to Horizontal Plane
   (b) Perpendicular to vertical plane
   (c) Perpendicular to Horizontal Plane and is of lowest order
   (d) Perpendicular to Horizontal Plane and is of Highest order
2. Total number of symmetry elements present in HCl molecule
   (a) 3 (b) ¥ (c) 4 (d) 2
3. The symmetry group is C_2 for the molecule/ion
   (a) H_2O (b) H_2O_2 (c) SO_2 (d) NO_2^-
4. How many C_2 are present in S_4N_4?
   (a) 1 (b) 2 (c) 3 (d) 4
5. What is the principle axis in H_2O molecule
   (a) C_2 (b) C_3 (c) C_4 (d) None of these
6. Molecule which contain centre of symmetry
   (a) Ethene (b) HCl (c) NH_3 (d) SF_4
7. Molecule which contain centre of symmetry
   (a) Ethene (b) XeF_4 (c) XeF_2 (d) All of these
8. The number of C_2 axes is SF_6 are,
   (a) 6 (b) 3 (c) 9 (d) 12
9. Which of the following matched incorrectly?

	Symmetry	Maximum no. that any molecule poses
(a)	S_2	1
(b)	i	1
(c)	σ_h	1
(d)	C_2	infinite

10. Which of the following molecule or ions poses an inversion centre?
    (a) $[PF_6]^-$ (b) SiH_4 (c) BF_3 (d) PF_5

11. Which of the following statement is incorrect regard a chiral molecule.
    (a) It has superimposable mirror image (b) lack of centre of symmetry
    (c) lack of alternate axis of symmetry (d) All of the above
12. For an octahedron, number of C_3 axis is
    (a) 0 (b) 3 (c) 4 (d) 8
13. Which of the following does not contain a C_3 axis?
    (a) $POCl_3$ (b) $[NH_4]^+$ (c) $[H_3O]^+$ (d) ClF_3
14. Which of the following species posses both C_3 and C_2 axis?
    (a) SO_3 (b) NH_3 (c) PCl_3 (d) $[H_3O]^+$
15. Which of the following molecule or ions possesses a C_4 principal axis?
    (a) XeF_4 (b) CF_4 (c) SF_4 (d) $(PF_4)^+$

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QUANTA CHEMISTRY

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ANSWER KEY
DPP-(3) GROUP THEORY

1. (d)	6. (a)	11. (a)
2. (b)	7. (d)	12. (c)
3. (b)	8. (c)	13. (d)
4. (c)	9. (c)	14. (a)
5. (a)	10. (a)	15. (a)

QUANTA CHEMISTRY

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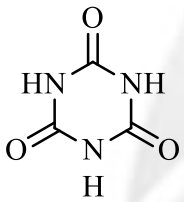
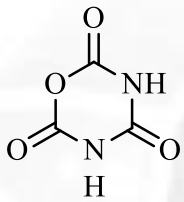
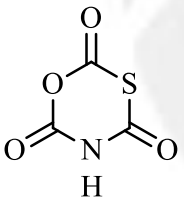
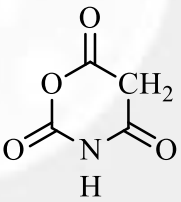
DPP-(4) GROUP THEORY

1. What is principal axis in triangle
   (a) C_2 (b) C_3 (c) C_4 (d) None of these
2. What is principle axis in square
   (a) C_2 (b) C_3 (c) C_4 (d) None of these
3. What is the principal axis in $POCl_3$?
   (a) C_5 (b) C_4 (c) C_5 (d) C_2
4. Out of the following molecules which one contains maximum symmetry operations

   (a) 

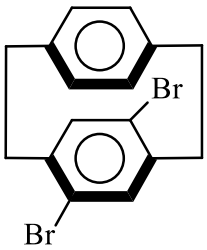
   (b) 

   (c) 

   (d) 

5. Which of the following is correct?
   (a) $C_2^z \times \sigma_{xz} = E$ (b) $C_2^z \times \sigma_{xz} = C_2^z$
   (c) $C_2^z \times \sigma_{yz} = \sigma_{yz}$ (d) $C_2^z \times \sigma_{xz} = \sigma_{yz}$
6. A molecule has a 2-fold axis and a mirror perpendicular to that. The point group must have a:
   (a) S_4 axis
   (b) Center of inversion
   (c) s_d plane
   (d) s_V plane
7. $[Co(en)_3]^{3+}$ ion ("en" denotes ethylene diamine) shows optical activity because it has:
   (a) An asymmetric carbon atom
   (b) No S_n axis of symmetry
   (c) A C_3 axis of symmetry
   (d) A C_2 axis of symmetry perpendicular to C_2 axis

8. The correct statement about the following molecule is



(a) Molecule is chiral and possesses a chiral plane

(b) Molecule is chiral and possesses a chiral axis

(c) Molecule is chiral and possesses a plane of symmetry

(d) Molecule is chiral and possesses a centre of symmetry

9. Match list-I (molecule) with List-II (shape) and select the correct answer using the codes given below the lists:

	List-I		**List-II**
I.	P_4	P.	Crown
II.	S_8	Q.	Polymeric (Dimeric)
III.	$AlCl_3$	R.	Tetrahedral
IV.	PCl_5	S.	Linear
		T.	Trigonal bipyramid

(a) I-R, II-P, III-Q, IV-T (b) I-P, II-R, III-Q, IV-T

(c) I-P, II-Q, III-R, IV-S (d) I-R, II-P, III-S, IV-T

10. $[Co(en)_3]^{3+}$ ion shows optical activity because it has

(a) An asymmetric C-atom (b) No S_n axis of symmetry

(c) A C_3 axis of symmetry (d) A $C_2 \perp$ to C_3

11. The point group of H_2O_2 (planar) is:

(a) C_{2v} (b) D_{2d} (c) C_{2h} (d) C_{3h}

12. The point group of 1, 3, 5, 7-tetraflurocyclo-octetraene is:

(a) D_{2d} (b) S_4 (c) C_2 (d) C_1

13. The symmetry point group of propyne is

(a) C_3 (b) C_{3V} (c) D_3 (d) D_{3d}

14. The point group of NSF_3 is:

(a) D_{3d} (b) C_{3h} (c) D_{3h} (d) C_{3v}

15. An AX_6 molecules belongs to the O_h group. The molecule is modified to AX_5Y. The point group changes to:

(a) D_{4h} (b) D_{6h} (c) C_{4h} (d) C_{4v}

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QUANTA CHEMISTRY

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ANSWER KEY
DPP-(4) GROUP THEORY

1. (b)
3. (a)
4. (a)
5. (d)
6. (b)
7. (b)
8. (a)
9. (a)
10. (b)
11. (c)
12. (a)
13. (b)
14. (d)
15. (d)

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DPP-(5) GROUP THEORY

1. Bipridyl (q = 90) belongs to the point group

   (a) C_s (b) C_{5h} (c) C_2 (d) C_{2v}

2. Ethylene molecule belong to the

   (a) D_{2h} (b) C_{2h} (c) C_{3v} (d) $C_{\infty h}$

3. $H_2SO_4 \xrightarrow{H_2O} A + 2H^+$, the point group of 'A' is:

   (a) C_s (b) T_d (c) O_h (d) None of these

4. The point group of Boric acid (non-planar) is P:

   (a) C_3 (b) C_{3v} (c) C_{3h} (d) None of these

5. Molecule belong to D_{3d} piont group:

   (a) Ferrocine (b) Staggered ethane

   (c) Staggered chromocene (d) Staggered ferrocene

6. Ethyne molecule belong to the

   (a) D_{2h} (b) C_{2h} (c) C_{2v} (d) $D_{\infty h}$

7. Tetrafluoro cubane belong to the point group.

   (a) D_{3d} (b) T_d (c) D_{2h} (d) D_{2d}

8. $NH_3 + HCl \xrightarrow{\text{Aqueous}} A + Cl^{\ominus}$, the point group of 'A' is:

   (a) C_s (b) T_d (c) O_h (d) None of these

9. Trans, 1, 2 difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre. If two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be:

   (a) C_1 (b) C_{2h} (c) C_{2v} (d) D_{2h}

10. $[B_{12}H_{12}]^{2-}$ belongs to the point group:

    (a) O_h (b) T_d (c) C_{2v} (d) I_h

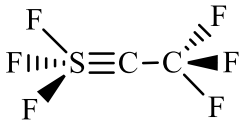
11. The molecule CO_2 belongs to the point group:

    (a) C_{2v} (b) C_{2h} (c) $D_{¥h}$ (d) D_{2h}

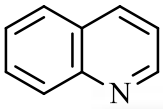
12. Trans, 1, 2 difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre. The point group of the molecule is:

    (a) C_1 (b) C_{2h} (c) C_{2v} (d) D_{2h}

13. The point group of is:



(a) D_{3d} (b) C_{3v} (c) C_s (d) C_1

14.  belongs to the point group:

(a) O_h (b) C_s (c) C_i (d) C_{2v}

15. 'B_2H_6' belong to the point group.

(a) D_{3d} (b) T_d (c) D_{2h} (d) D_{2d}

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ANSWER KEY
DPP-(5) GROUP THEORY

1. (c)
2. (a)
3. (b)
4. (a)
5. (b)
6. (d)
7. (b)
8. (b)
9. (d)
10. (d)
11. (c)
12. (c)
13. (c)
14. (b)
15. (c)

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DPP-(6) GROUP THEORY

1. What is the point group of $Fe_2(CO)_9$?

   (a) C_{3h} (b) D_{3h} (c) C_{3v} (d) D_{3d}

2. D_{nd} point group contain:

   (a) E, C_n, nC_2, $n\sigma_d$, S_{2n}, i

   (b) E, C_n, $nC_2 \perp n\sigma_d$, S_{2n}, i

   (c) E, C_n, $nC_2 \perp C_n$, $n\sigma_d$, S_{2n}

   (d) E, C_n, $C_2 \perp n\sigma_d$, S_{2n}, i

3. Write the matrix representing final coordinate after doing operation of inversion centre (i).

   (a) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (b) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

   (c) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (d) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

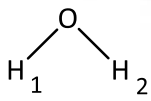
4. A molecule contain C_4 principal axis of symmetry and also contain s_h plane of symmetry. If the point group of the molecule is D_{4h} than molecule contain:

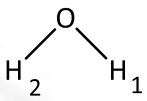
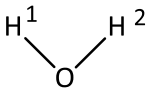
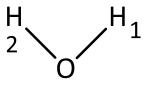
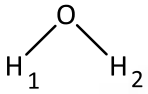
   (a) $E + C_4 + 4C_2 + S_8$

   (b) $E + C_4 + 4C_2 \perp C_4$, s_n only

   (c) $E + C_4 + s_h + 4C_2 + S_4 + i + 4s_b$

   (d) None of these

5. What is final structure of  after performing inversion centre.

   (a)  (b)  (c)  (d) 

6. Match the column-I with column-II

	Column-I		Column-II
I.	$Ir_4(CO)_{12}$	P.	T_d
II.	S_4N_4	Q.	C_{3v}
III.	S_8	R.	D_{2d}
IV.	$POCl_3$	S.	D_2

		T.	D_{3h}
		U.	D_{4d}

(a) I-P, II-S, III-U, IV-Q (b) I-P, II-R, III-U, IV-Q

(c) I-S, II-R, III-U, IV-Q (d) I-S, II-Q, III-R, IV-S

7. The point group of chair conformer of chlorocyclohexane:

(a) C_s (b) D_{3d} (c) C_{2v} (d) C_{3v}

8. Match List-I with List-II and select the correct answer using the codes given below the lists:

	List-I		List-II
(P)	$[Cu(H_2O)_6]^{2+}$	1.	C_{3v}
(Q)	$Fe_2(CO)_9$	2.	D_{3h}
(R)	Eclipsed ferrocene	3.	O_h
I		4.	D_{3d}
		5.	D_{5h}
		6.	D_{4h}

(a) P-3, Q-2, R-5 (b) P-6, Q-4, R-5

(c) P-6, Q-2, R-5 (d) P-3, Q-6, R-4

9. The point group of ClF_3 molecule and its corresponding number of irreducible representation are respectively

(a) C_{3v} and 4 (b) C_{2v} and 4

(c) C_{3v} and 3 (d) C_{2v} and 3

10. The product $C_2^x\sigma_{xy}$ (C_2^x is the two-fold rotation axis around the x-axis and σ_{xy} is the xy mirror plane) is

(a) σ_{xz} (b) σ_{yz} (c) C_2^y (d) C_2^z

11. The correct relation involving symmetry operations

(a) $S_4^2 = S_2$ (b) $\sigma(xz)\sigma(yz) = C_2(x)$

(c) $S_4^3 = C_4^3$ (d) $S_6^3 = S_2$

12. The molecule that possesses S_4 symmetry element is

(a) ethylene (b) allene (c) benzene (d) 1, 3-butadiene

13. The low temperature (–98ºC) ^{19}F NMR spectrum of SF_4 shows doublet of triplets. It is consistent with the point group symmetry

(a) C_{3v} (b) C_{4v} (c) T_d (d) C_{2v}

14. Which of the following do not posses C_{2h} point group?

(a) trans $[CO(en_2Cl]^+$ (b) 1, 2 dichloroethylene (cis)

(c) 1, 2 dichloroethylene (trans) (d) difluorobenzene

15. Which of the following symmetry element is present in "T" point group.

(a) proper axis of rotation (b) Improper axis of rotation

(c) Centre of inversion (d) Plane of symmetry

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ANSWER KEY
DPP-(6) GROUP THEORY

1. (b)
2. (c)
3. (d)
4. (c)
5. (c)
6. (b)
7. (a)
8. (c)
9. (b)
10. (a)
11. (d)
12. (b)
13. (d)
14. (b)
15. (a)

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DPP-7 GROUP THEORY

1. D_{nd} piont group contain:
   (a) E, C_n, nC_2, $n\sigma_d$, S_{2n}, i
   (b) E, C_n, $nC_2 \perp n\sigma_d$, S_{2n}, i
   (c) E, C_n, $nC_2 \perp C_n$, $n\sigma_d$, S_{2n}
   (d) E, C_n, $C_2 \perp n\sigma_d$, S_{2n}, i
2. A molecule contain C_4 principal axis of symmetry and also contain σ_h plane of symmetry. If the point group of the molecule is D_{4h} than molecule contain:
   (a) $E + C_4 + 4C_2 + S_8$
   (b) $E + C_4 + 4C_2 \perp C_4$, σ_n only
   (c) $E + C_4 + \sigma_h + 4C_2 + S_4 + i + 4\sigma_b$
   (d) None of these
3. Match the column-I with column-II

Column-I	Column-II
I. $Ir_4(CO)_{12}$	P. T_d
II. S_4N_4	Q. C_{3v}
III. S_8	R. D_{2d}
IV. $POCl_3$	S. D_2
	T. D_{3h}
	U. D_{4d}

   (a) I-P, II-S, III-U, IV-Q
   (b) I-P, II-R, III-U, IV-Q
   (c) I-S, II-R, III-U, IV-Q
   (d) I-S, II-Q, III-R, IV-S
4. The point group of chair conformer of chlorocyclohexane:
   (a) C_s (b) D_{3d} (c) C_{2v} (d) C_{3v}
5. Match List-I with List-II and select the correct answer using the codes given below the lists:

List-I	List-II
(P) $[Cu(H_2O)_6]^{2+}$	1. C_{3v}
(Q) $Fe_2(CO)_9$	2. D_{3h}
(R) Eclippsed ferrocene	3. O_h
	4. D_{3d}
	5. D_{5h}
	6. D_{4h}

   (a) P-3, Q-2, R-5 (b) P-6, Q-4, R-5 (c) P-6, Q-2, R-5 (d) P-3, Q-6, R-4

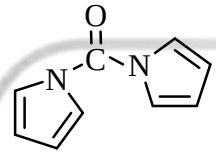
6. The low temperature (–98°C) ^{19}F NMR spectrum of SF_4 shows doublet of triplet. It is consistent with the point group symmetry.
(a) C_{3v} (b) C_{4v} (c) T_d (d) C_{2v}

7. The symmetry elements that are present in BF_3 are:
(a) C_3, σ_v, σ_h,$3C_2$ (b) C_3, $3C_2$, S_2, σ_v (c) C_3, $3C_2$, σ_h, S_2 (d) C_3, σ_v, σ_v, i

8. The symmetry point group of the most stable geometry of the following molecule Cl(H)C = C = C(H)Cl is:
(a) C_2 (b) C_1 (c) C_{2v} (d) C_{2h}

9. List all the symmetry elements in cyclooctatetraene?
(a) E, C_2 $2C_2^1$, σ_d (b) E, C_4 $4C_2^1$, σ_d S_8
(c) S_4, C_2 , E, $2\sigma_d$, $2C_2^1$ (d) E S_4 C_2 C_2^1 σ_d

10. To what point group does the following molecule belong ?



(a) C_2 (b) C_i (c) C_{2h} (d) C_{2v}

11. Which of the following symmetry element is present in "T" point group.
(a) proper axis of rotation (b) Improper axis of rotation
(c) Centre of inversion (d) Plane of symmetry

12. Which of the following do not posses C_{2h} point group?
(a) trans $[CO(en)_2Cl]^+$ (b) 1, 2 dichloroethylene (cis)
(c) 1, 2 dichloroethylene (trans) (d) difluorobenzene

13. The low temperature (–98ºC) ^{19}F NMR spectrum of SF_4 shows doublet of triplets. It is consistent with the point group symmetry
(a) C_{3v} (b) C_{4v} (c) T_d (d) C_{2v}

14. The molecule that possesses S_4 symmetry element is
(a) ethylene (b) allene (c) benzene (d) 1, 3-butadiene

15. The correct relation involving symmetry operations
(a) $S_4^2 = S_2$ (b) $\sigma(xz)\sigma(yz) = C_2(x)$
(c) $S_4^3 = C_4^3$ (d) $S_6^3 = S_2$

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ANSWER KEY

1 (c)
2. (c)
3. (b)
4. (a)
5. (c)
6. d)
7. (a)
8. (a)
9. (c)
10. (d)
11. (a)
12. (b)
13. (d)
14. (b)
15. (d)

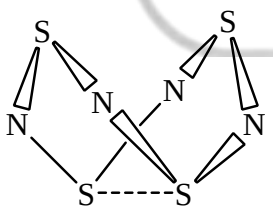
Hints and Solutions

1. D_{nd}, point group can be extended as

$D_{nd} \rightarrow E + C_n + nC_2 + n\sigma_d + S_{2n}$

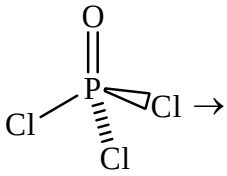
2. D_{4h}, can be extended as

$D_{4h} \rightarrow E + C_4 + 4C_2 + 4\sigma_v + \sigma_h + S_4 + S_2$

3. S_4N_4  – D_{2d}

extreme cradle structure

S_8 – crown shape, D_{4d}-point group

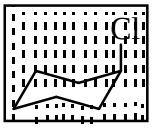
$POCl_3$ – 

C_3-axis ✓
$3C_2$-axis ×
$3\sigma_v$ ✓

C_{3v} – point group

$Ir_4(CO)_{12} \rightarrow$ Tetrahedral structure

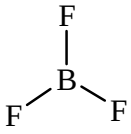
T_d-point group

4.  Only plane of symmetry

5.

$Fe_2(CO)_9$	Eclipsed ferrocene	$[Cu(H_2O)_6]^{+2}$
C_3-axis ✓	C_5-axis ✓	C_4-axis ✓
$3C_2$-axis ✓	$5C_2$-axis ✓	$4C_2$-axis ✓
σ_h ✓	σ_h ✓	σ_h ✓
D_{3h}	D_{5h}	D_{4h}

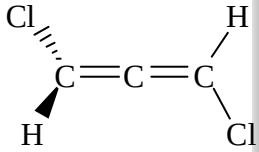
6. Correct option is d.

7. 

Point group: D_{3h}

It contans C_3, $3C_2$, σ_h, S_3, $3\sigma_v$

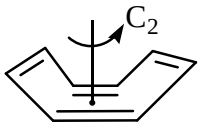
The symmetry elements matched with option (a)

8. 

This molecule is chiral

Therefore, no plane, only one C_2.

Correct option is (a)

9. 

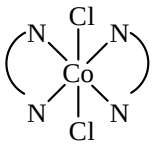
Point group, D_{2d}, has C_2, $2 \perp C_2^1$, $2\sigma_d$, S_4, E

10. It contains a C_2 axis as principal axis, which in contained by a place which bisect the molecule hence the point group in C_{2v}.

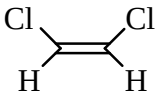
Correct answer (d)

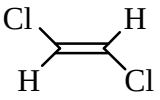
11. The point group "T" has 4 C_3 axis and $3C_2$ axis of symmetry only.

12. trans $[Co(en)_2Cl]^+$

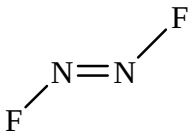
 Point group C_{2h}

1,2 dichloroethylene (cis) 1,2 dichloroethylene (trans)

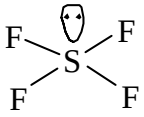

: C_{2v}

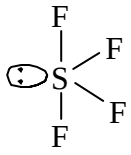

: C_{2h}

difluorobenzene:


: C_{2h}

13. Possible structure of SF_4 are

(i)  but it only give one signal in ^{19}F NMR, because all F-atom are equivalent.

(ii)  This give doublet of triplets, due to two different kind of fluorine atoms. This structure contain

C_2 ✓
$2C_2$ ✗
σ_h ✗
$2\sigma_v$ ✓
→ C_{2v}

14. Only allene having D_{2d} point group contains S_4–symmetry element.

15. $S_4^2 = C_4^2 \times \sigma^2 \rightarrow C_2 \times E \rightarrow C_2$

$\sigma_{xx}\sigma_{yz} = C_{2Z}$

$S_4^3 = C_4^3 \times \sigma^3 \rightarrow C_4^3 \times \sigma \rightarrow S_4^3$

$S_6^3 = C_6^3 \times \sigma^3 \rightarrow C_2 \times \sigma \rightarrow S_2$

Correct option is 'd'

× × × × ×

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DPP-8 GROUP THEORY

1. The S_2 operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to:

   (a) (–x, –y, z) (b) (x, –y, –z) (c) (–x, y, –z) (d) (–x, –y, –z)

2. The result of the product $C_2(x)\ C_2(y)$ is

   (a) E (b) σ_{xy} (c) $C_2(z)$ (d) i

3. Write down the matrix representing a two-step transformation of a general point (x, y, z): rotation through 180° (about the z-axis) followed by reflection in an yz mirror plane:

   (a) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (b) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (c) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ (d) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

4. A molecule having T_d point group with 24 symmetry operations, if centre of symmetry added to this point group, the resultant point group will look like

   (a) T_d (b) T (c) T_i (d) T_h

5. In a pyramidal molecule AB_3 if one B atom is replaced by X-atom, then point group of the resultant molecule will

   (a) C_{2v} (b) C_{3v} (c) C_1 (d) C_s

6. The product σ_{xy}, S_4^2 (S_4^2 is the four fold improper axis of rotation around the z axis, and σ_{xy} is the reflection in the xy plane is).

   (a) C_4^z (b) $C_4^i\, i$ (c) C_4^y (d) C_2^z

7. Transformation matrix for clockwise rotation of unit vector along x, y, z direction by an angle ‘θ’, with respect to the y-axis is

   (a) $\begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & -1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$ (b) $\begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}$

(c) $\begin{bmatrix} \sin\theta & 0 & \cos\theta \\ 0 & 1 & 0 \\ -\cos\theta & 0 & \sin\theta \end{bmatrix}$ (d) $\begin{bmatrix} \sin\theta & 0 & -\cos\theta \\ 0 & 1 & 0 \\ \cos\theta & 0 & \sin\theta \end{bmatrix}$

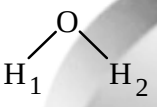
8. Which of the following is not equal to the identity?
(a) $(\sigma)^2$ (b) C_2^2 (c) i (d) None

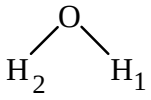
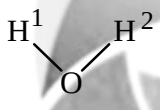
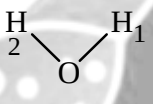
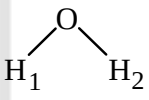
9. What is the point group of five pointed star.
(a) D_{6h} (b) D_{5h} (c) C_{6v} (d) C_{6v}

10. What is the point group if the sharpened natraj pencil?
(a) $D_{\infty h}$ (b) $D_{\infty d}$ (c) $C_{\infty v}$ (d) $C_{\infty h}$

11. Write the matrix representing final coordinate after doing operation of inversion centre (i).

(a) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (b) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (c) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (d) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

12. What is final structure of  after performing inversion centre.

(a)  (b)  (c)  (d) 

13. What is the point group of $Fe_2(CO)_9$?
(a) C_{3h} (b) D_{3h} (c) C_{3v} (d) D_{3d}

14. The product $C_2^x\sigma_{xy}$ (C_2^x is the two-fold rotation axis around the x-axis and σ_{xy} is the xy mirror plane) is
(a) σ_{xz} (b) σ_{yz} (c) C_2^y (d) C_2^z

15. The point group of ClF_3 molecule and its corresponding number of irreducible representation are respectively
(a) C_{3v} and 4 (b) C_{2v} and 4 (c) C_{3v} and 3 (d) C_{2v} and 3

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ANSWER KEY

1 (d)
2. (c)
3. (a)
4. (d)
5. (d)
6. (a)
7. (a)
8. (c)
9. (b)
10. (c)
11. (d)
12. (c)
13. (b)
14. (a)
15. (b)

Hints and Solutions

1. S_2 is equivalent to inversion centre (i)

$i\,(x, y, z) = (-x, -y, -z)$

2. $C_{2x}C_{2y}\,(x\ y\ z) \longrightarrow C_{2x}(-x\ y\ -z)$

$\downarrow$

$(-x\ -y\ z) \longleftarrow C_{2z}(x\ y\ z)$

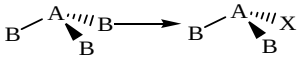
3. $C_{2z}\,(x, y, z) \rightarrow (-x, -y, z)$

$\downarrow \sigma_{yz}$

$(x, -y, z)$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

4. If centre of symmetry added to this point group, the resultant point group will look like T_h.



5. contain only plane of symmerty passing through AX reflecting the 2B's. Hence point group of C_s.

6. $\sigma_{xy}S_4^z$

$= \sigma_{xy}\sigma_{xy}C_4^z$

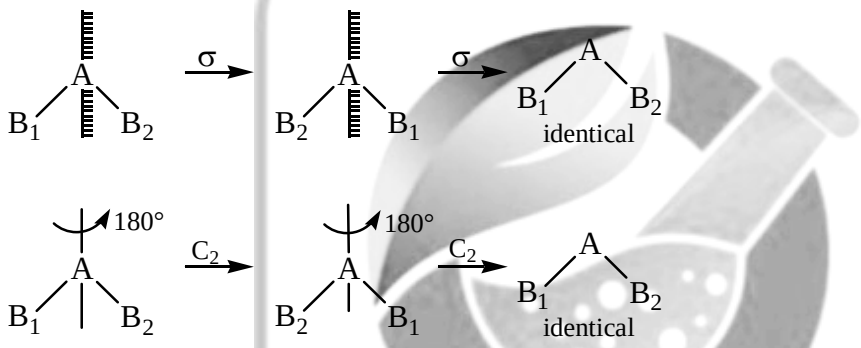
$= \sigma_{xy}{}^2C_4^z$

$= EC_4^z$

$= C_4^z$

Correct option is (a)

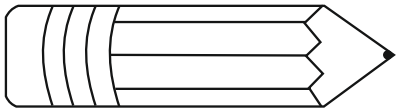
7. $\begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & +1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$

8. 

but inversion centre does not give identical structure hence correct option (c).

9. There is a 5 fold rotation axis perpendicular to the plane of the page. There are $5C_2$ perpendicular to the principal rotation axis, so this is a D'group. There is a mirror plane in the plane of page, so point group D_{5h}.

5 pointed star

10. 

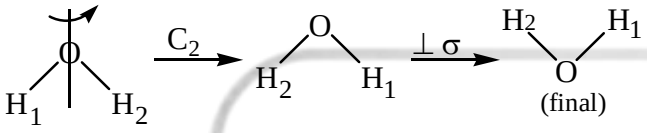
This linear shape has C infinity rotation axis along the axis of the pencil and no inversion centre. Therefore pencil is $C_{\infty v}$

11. Applying inversion centre, the coordinate of the system inverts to 180°, hence applying *i* to

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

given $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

12. To get final structure the following operation must be applied



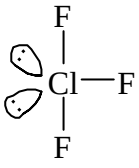
13. $Fe_2(CO)_9$ contains

C_3 ✓
$3C_2$ ✓ → D_{3h}
σ_h ✓

14. $C_{2x}\sigma_{xy}(x,y,z) = C_{2x}(x,y,-z)$

$= (x,-y,z)$

which is equivalent to σ_{xz}

15. 

It contains

C_2 ✓
$2C_2$ ✗
σ_h ✗
$2\sigma_v$ ✓ → C_{2v}

C_{2v} –point group have 4–class, it means, it have 4 irreducible representations (According to first postulate of GOT)

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DPP-9 GROUP THEORY

1. Which of the following matrix represents the rotation of molecule about z-axis?

(a) $\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & \theta & 1 \end{bmatrix}$ (b) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & 0 \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$

(c) $\begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}$ (d) $\begin{bmatrix} \cos 2\theta & \sin 2\theta & 0 \\ -\sin 2\theta & \cos 2\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$

2. Write down the matrix representing a two-step transformation of general point (x, y, z); rotation through 180°C (about the z-axis) followed by reflection in an yz mirror plane:

(a) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (b) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (c) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ (d) $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

3. If order of the group is H and that of the subgroup is G, then correct among the following is, where K is an integer positive value K > 1

(a) H = KG (b) G = KH (c) GH = K (d) None

4. D_{1d} point group is equivalent to the symmetry point group provided below

(a) C_2 (b) C_{2v} (c) C_{2h} (d) D_2

5. A molecule contains the following symmetry operations E, $2C_6$, $2C_3$, $3\sigma_d$, & $3\sigma_v$. The number of classes and order of the symmetry point group is:

(a) 3, 12 (b) 5, 12 (c) 6, 12 (d) 6, 6

6. The number of classes present in C_{4v} point group is:

(a) 4 (b) 5 (c) 6 (d) 8

7. $[CoCl_4]^{2-}$ is a blue coloured complex. Controlled treatment of this complex with water generates two isomeric light pink colour complexes of composition $[Co(H_2O)_4Cl_2]$

Identify the correct point groups for $[CoCl_4]^{2-}$ and two isomeric complexes $[Co(H_2O)_4Cl_2]$.

(a) D_{2h} and (C_{2v} and C_{2h}) (b) T_d and (C_{2v} and D_{4h})

(c) D_{4h} and (C_{2v} and D_{4h}) (d) T_d and (C_{2v} and C_{4v})

8. Trans 1,2-difluoroethylene molecule has a 2-fold rotational aixs, a symmetry plane perpendicular to the rotational axis and an inversion centre.

The number of irreducible representations of the point group of the molecule is

(a) 1 (b) 2 (c) 3 (d) 4

9. The property that is not required (necessarily) for a group.

(a) Closure (b) Commutativity (c) associativity (d) Identity element

10. Conversion of boron trifluride to tetrafluoroborate accompanies:

(a) Increase in symmetry and bond elongation. (b) Increase in symmetry and bond contraction

(c) Decrease in symmetry and bond contraction (d) Decrease in symmetry and bond elongation.

11. How many classes of symmetry operation are in the C_{2v} point group ?

(a) 2 (b) 3 (c) 4 (d) 5

12. What is the muliken symbol for the following IRR

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
Γ_1	1	1	–1	–1	–1	1

(a) A_1' (b) A_1'' (b) A_2' (d) A_2''

13. Identify the mulliken symbol

Γ	E	C_n	nC_2	i	σ_n
	1	1	–1	–1	–1

(a) A''_g (b) B''_u (c) A'_{2u} (d) A''_{2u}

14. What is the character of the $S_4(z)$ (clockwise rotation) operation, if x, y, z coordinate are used as the bases?

(a) 1 (b) 2 (c) 0 (d) –1

15. A square pyramidal, MX_4, molecule belongs to C_{4v} point group. The symmetry operations are: E, $2C_4$, C_2, $2\sigma_v$ and $2\sigma_d$. The trace for the reducible representation, when symmetry operations of C_{4v} applied to MX_4, is.

(a) 5 1 1 1 3 (b) 1 1 1 1 1 (c) 5 1 1 1 1 (d) 4 1 1 1 3

× × × ×

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ANSWER KEY

1 (a)
2. (a)
3. (a)
4. (c)
5. (c)
6. (b)
7. (b)
8. (d)
9. (b)
10. (a)
11. (c)
12. (d)
13. (d)
14. (d)
15. (a)

Hints and Solutions

1. $C_{nz} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$

2. $C_{2z}\,(x, y, z) \rightarrow (-x, -y, z)$

$\downarrow \sigma_{yz}$

$(x, -y, z)$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

3. If order of the group is H and that of the subgroup is G, then
H = KG

4. D_{1d} contains C_1 , $1C_2$, S_2, σ_d(perpendicular to C_2). These are the same symmetry element which also make C_{2h} point group.

5. Number of classes in a character table of any point group is equal to the number of distinct symmetry operation.

So, the given distinct symmetry operations are 6 in number (E, $2C_6$, $2C_3$, C_2, $3\sigma_d$, $3\sigma_v$).

From the given symmetry operation the point group is C_{6V}.

Hence, order = 6 × 2 = 12

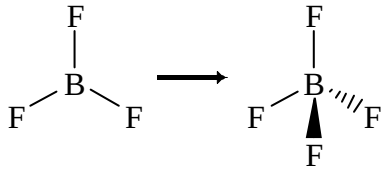
6. C_{4v} contain E, $2C_4$, C_2, $2\sigma_v$, $2\sigma'_v$ as distinct operation. Hence 5 classes.

7. $[CoCl_4]^{2-}$ have tetrahedral structure, so its point group is T_d.

$[Co(H_2O)_4Cl_2]$ has two structures cis and trans, having C_{2v} and D_{4h} point group. respectively.

8. Number of IRR = Classes in the point group C_{2h} have four classes, so number of IRR are 4.

9. A group must posses property like closure, associativity and should have identity element.

10. 

(planar) (Td)

Converting from planar to tetrahedral intend to increased the symmetry and due to decrease in the %s character there is bond elongation.

11. There 4 classes: 1 (E), 1 (C_2), 1 ($\sigma_{v(yz)}$, 1 $\sigma'_{v(xz)}$.

12. Symmetric wrt C_3 the principal axis then A, asymmetric wrt to subsidiary axis C'_1 then A_2 and asymmetric wrt to σ_n then double dash, so muliken symbol is A''_2.

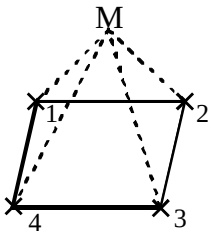
13. 1. Symmetric wrt C_n (principal axis) : A
2. Assymmetric wrt $^nC_2$ (subsidiary) : A_2
3. Assymmetric wrt "i" ; A_{2u}
4. Assymmetric wrt $\sigma_h = A''_{2u}$

14. $\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

character = 0 + 0 – 1 = –1

15. Square Pyramidal MX_4 molecule $\rightarrow C_{4v}$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
	5	1	1	1	3



C_4 passes through M $\boxed{C_4^2 = C_2}$

one $\sigma_d \rightarrow$ contains MX_1X_3 & reflects X_2 and X_4 & other σ_d contains MX_2X_4 and reflects X_1dX_3

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DPP-10 GROUP THEORY

1. Select correct statement regarding C_{3v} point group.

   1. Order of the group is 6.

   2. Class of the group is 3 (E, $2C_3$ and $3\sigma_v$)

   3. Number of irreducible representations 3 (A_1, A_2, E).

   (a) 1 and 2 (b) 1 and 3 (c) 2 and 3 (d) 1, 2 and 3

2. A molecule contains the following symmetry operations: E, $2C_6$, $2C_3$, C_2, $3\sigma_d$, $3\sigma_v$. Thenumber of classes and order of the symmetry point group is:

   (a) 3, 12 (b) 5, 12 (c) 6, 12 (d) 6, 6

3. The character of the irreducible representation A_1 in C_{2v} piont group is given below:

	E	C_2	σ_v	σ_v'
A_1	1	1	1	1

   Identify, one irreducible representation orthogonal to A_2 among the following:

	E	C_2	σ_v	σ_v'
Γ_1	1	–1	1	1
Γ_2	1	–1	–1	1
Γ_3	1	1	1	–2
Γ_4	1	–1	1	2

   (a) Γ_1 (b) Γ_2 (c) Γ_3 (d) Γ_4

4. Correct statement among the following were

   I. All the element in the group C_n commute with each other.

   II. Point group of Boric acid is D_{3h}

   III. S_8 molecule containing S_8 improper axis of rotation

   (a) I, II (b) I, III (c) II, III (d) All are correct

5. If one B-atoms in tetrahedral molecule AB_4 are exchanged by -atoms, then number of classes in the point group of resultant molecule were

(a) 6 (b) 8 (c) 4 (d) 3

6. Incorrect statement among the following is

I. $C_n^{n+1} = C_n$

II. If S_n exist in a molecule, then C_n must exist in the molecule.

III. A proper rotation axis of even order and a perpendicular reflection plane generate an inversion centre, i.e. $C_{2n}^{n}\sigma = i$

(a) I, II, III (b) I, III (c) II, III (d) I, II

7. Choose appropriate answer:

(i) C_{2v} is an example of an abelian group. (ii) C_{2v} is present in nonbornane.

(a) Only (i) is correct (b) Only (ii) is correct (c) Both are correct (d) None is correct

8. If the displacement vectors of all atoms in cis-butadiene are taken as the basic vectors the characters of the reducible representation of E, C_2, σ_v (molecular plane) aid σ'_v are:

(a) 30, 10, 30, 0 (b) 30, 0, 10, 0 (c) 30, 20, 0, 0 (d) 30, 0, 20, 0

9. The point group of ClF_3 molecule and its corresponding number of irreducible representation are respectively:

(a) C_{3v} and 4 (b) C_{2v} and 4 (c) C_{3v} and 3 (d) C_{2v} and 3

10. Which of the following statement is not true?

(a) A and B represent muliken symbol for 1-D IRR

(b) E represent muliken symbol for 2-D IRR

(c) T represent muliken symbol for 3-D IRR

(d) None of these

11. What is the trace of the matrix for $C_3(z)$ (clockwise rotation) operation if x, y, z coordinate are used are the bases.

(a) 1 (b) –1 (c) 0 (d) 2

12. Which of the following is correct regarding reciprocal of the product of groups?

(a) $(ABC)^{-1} = B^{-1}C^{-1}A^{-1}$ (b) $(ABC)^{-1} = A^{-1}C^{-1}C^{-1}$

(c) $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$ (d) $(ABC)^{-1} = B^{-1}A^{-1}C^{-1}|$

13. Character table of C_{2v}, point group is

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	1
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y

If the initial and final states belong to A_1 to B_1 irreducible representation respectively, the allowed electronic transition A_1 to $B_{\backslash 1}$ is:

(a) z-polarized (b) y-polarized (c) x-polarized (d) x, z-polarized

14. A molecules contains the following symmetry operations: E, $2C_6$, $2C_3$, C_2, $3\sigma_d$, $3\sigma_v$. The number of classes and order of the symmetry point group is

(a) 3, 12 (b) 5, 12 (c) 6, 12 (d) 6, 6

15. Identify the Mulliken notation for the following irreducible representation

	E	C_n	nC_2	i	σ_h
	1	1	–1	–1	–1

(a) $A_{1u}^{'}$ (b) $A_{2u}^{''}$ (c) $B_{2u}^{'}$ (d) $A_{2u}^{'}$

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QUANTA CHEMISTRY

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ANSWER KEY

1 (d)
2. (c)
3. (b)
4. (b)
5. (d)
6. (b)
7. (c)
8. (b)
9. (b)
10. (d)
11. (c)
12. (c)
13. (c)
14. (c)
15. (b)

Hints and Solutions

1. $C_{3v} \rightarrow E + 2C_3 + 3\sigma_v$
order = 6, class = 3
$\Rightarrow$ Number of IRR = Class = 3

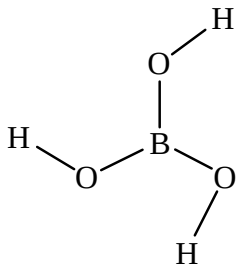
2. Molecule contain
$E + 2C_6 + 2C_3 + C_2 + 3\sigma_d + 3\sigma_v$
Classes = 6, order = 12

3.

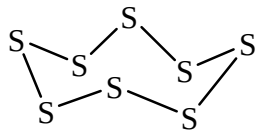
	E	C_2	σ_v	σ_v'
Γ_1	1	–1	1	1
Γ_2	1	–1	–1	1
Γ_3	1	1	1	–2
Γ_4	1	–1	1	2
A_1	1	1	1	1

Γ_1, $\Gamma_1 \times A_1 = 1 \times 1 \times 1 + 1 \times (-1) \times 1 + 1 \times 1 \times 1 + 1 \times 1 \times 1 = 2$
Γ_2, $\Gamma_2 \times A_1 = 1 \times 1 \times 1 + 1 \times (-1) \times 1 + 1 \times (-1) \times 1 + 1 \times 1 \times 1 = 0$

4. C_n is a abelian point group in which all element commute with each other.
H_3BO_3–Boric Acid



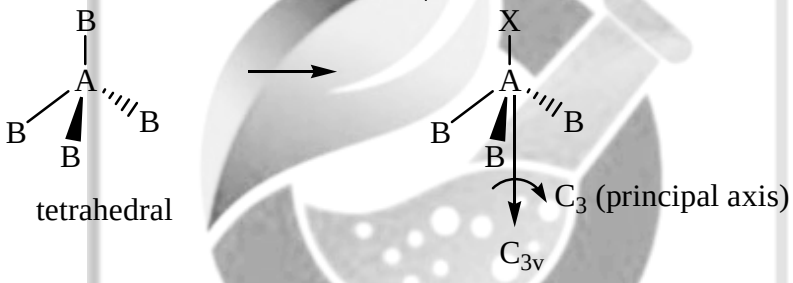
it contain C_3-axis and σ_h-mirror plane, so point group is C_{3h}.



have C_4 and have σ_d $4C_2$

So point group is D_{4d} and it contains S_8 also.

5. If one B-atoms in tetrahedral molecule AB_4 are exchanged by -atoms, then number of classes in the point



tetrahedral

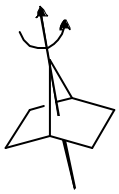
In the resulting molecule there are 3 plane each passing through Cl – C – H bond and containing the principal axis, this plane is known as vertical plane (σ_v) and C_{3v} point group has 3 classes.

6. $C_n^{n+1} = C_n^n . C_n^1 = E$ $C_n^1 = C_n$

It is not necessary for a molecule to have C_n axis if S_n is present in the molecule. For example Allene has S_4 axis but do not have C_4 axis.

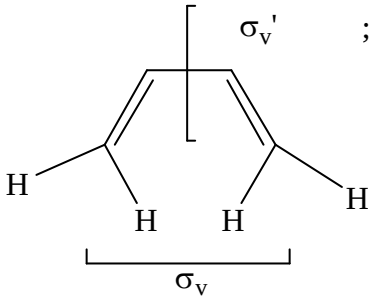
$C_{2n}^n \sigma = C_2^1 \sigma = S_2 = i$.

7. All the element in C_{2v} are commute with each other hence it is a abelian point group.

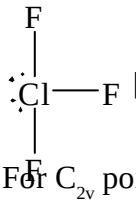


C_2 (Principal axis)

and contain σ_v has plane of symmetry so point group is C_{2v}.

8. 

C_{2v}	E	C_2	σ_v	σ_v'
Number of unshift atoms	10	0	0	10
Contribution per atom	3	–1	1	1
Reducible representation	30	0	10	0

9.  [C_2, $2\sigma_v$ hence, C_{2v} point group]

For C_{2v} point group, four irreducible representation

Correct option is (b)

10. Correct option (d), all statements are true.

11. The matrix representation of $C_3(z)$ is

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{trace} = -\frac{1}{2}-\frac{1}{2}+1=0$$

12. The reciprocal of the product of two or more elements is equal to the product of the reciprocal in reverse order

$(ABC..... XY)^{-1} = Y^{-1}X^{-1} .... C^{-1}B^{-1}A^{-1}$

13. $A_1 \times B_1 =$

$$\begin{array}{rcccc} A_1 & -1 & 1 & 1 & 1 \\ B_1 & -1 & -1 & 1 & -1 \\ \hline & 1 & -1 & 1 & -1 \end{array} \rightarrow B_1 \rightarrow X-\text{Plarized.}$$

$\Rightarrow$ A_1 to B_1 is X-Polarized

14. Molecules contains $\rightarrow E, 2C_6, 2C_3, C_2, 3\sigma_d, 3\sigma_v$

Classes = 6

Order = $1+2+2+1+3+3=12$

15.

	E	C_n	nC_2	i	σ_n
A''_{2u}	1	1	–1	–1	–1

$A \rightarrow$ sym. w.r. to C_η

$A_2 \rightarrow$ antisymm. w.r. to ηC_2

$u \rightarrow$ antisymm. w.r. to i

$'' \rightarrow$ antisymm. w.r. to σ_h

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DPP-11 GROUP THEORY

1. The reducible representation for all motions of the water molecule is reduce to:

(a) $3A_1 + 3A_2 + B_1 + 2B_2$ (b) $3A_1 + A_2 + 3B_2 + 2B_2$

(c) $A_1 + 3A_2 + B_1 + 2B_2$ (d) None of these

2.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, + z^2$
A_2	1	1	–1	R_z	$(x^2 – y^2, xy)$
E	2	–1	0	(x, y) (R_x, R_y)	(xz, yz)

C_{3v}	E	$2C_3$	$6\sigma_v$
Γ	12	0	2

Reduced Γ to its irreducible representations:

(a) $3A_1 + A_2 + 4E$ (b) $2A_1 + 2A_2 + 4E$ (c) $A_1 + 3A_2 + 4E$ (d) $3A_1 + 2A_2 + 3E$

3. Given the character table of the point group C_{3v}.

	E	$2C_3$	$3\sigma_V$	
A_1	1	1	1	s
A_2	1	1	–1	
E	2	–1	0	(x, y)

Consider irreducible representation, Γ

	E	$2C_3$	$3\sigma_V$
Γ	6	3	0

Its irreducible components are:

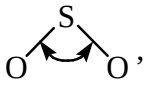
(a) $E + 2A_1 + 2A_2$ (b) $2E + A_1 + A_2$ (c) $3A_1 + 3A_2$ (d) $E + 2A_1$

4. Suppose that the characters of a reducible representation of the C_{2v} point group are $\chi(E) = 4$, $\chi(C_2) = 2$, $\chi(\sigma_v) = 0$ and $\chi(\sigma'_v) = 2$. This is usually expressed by writing $\Gamma = 4\ 2\ 0\ 2$. Determine how many times each irreducible representation of C_{2v} is contained in $\Gamma = 4\ 2\ 0\ 2$.

C_{2V}	E	C_2	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1
Γ	4	2	0	2

(a) $2A_1 + A_2 + B_2$ (b) $2A_2 + 2A_2 + B_2$ (c) $A_1 + 2A_2 + B_2$ (d) None of these

5. Given below, a double headed arrow with represent the bending mode for SO_2 molecule,



, this bending mode belongs to which of the following irreducible representation.

(a) A_2 (b) A_1 (c) B_2 (d) B_2

6. The third part of the character table gives us information about

(a) Mullikans's symbols.

(b) Characters of irreducible representations function.

(c) Rotations around X, Y, Z axes

(d) Transformation characteristic of quadratic

7. Refer to the character table of the point group C_{3v} given above. Find which of the following transition is forbidden:

(a) $a_2 \leftrightarrow a_1$ (b) $a_1 \leftrightarrow e$ (c) $a_2 \leftrightarrow e$ (d) $a_1 \leftrightarrow a_1$

8. For the irreducible representation

E	$2S_4$	$C_{2(z)}$	$2C'_2$	$2\sigma_d$
1	–1	1	1	1

(a) A_1 (b) B_1 (c) A_2 (d) B_2

9. For the irreducible representation

E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
2	–1	10	2	–1	0

(a) E_1' (b) E_2' (c) E' (d) E''

10. What are trace element of NH_3, use the character table given below

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0

(a) 4 0 1 (b) 3 1 2 (c) 3 2 1 (d) 4 1 2

11. A complete set of element that are conjugate to one another is called

(a) order (b) class (c) representation (d) None of the above

12. Consider the following table and replace Γ by correct Muliken rotation (take z as the principle axis z)

D_3	E	$3C_2$	$3C_2'$
Γ	+1	+1	−1

(a) A_2 (b) B_2 (c) B_1 (d) A_1

13. The irreducible representations of C_{2h} are A_g, B_g, A_u and B_u. The Raman active modes of trans-1, 3-butadiene belong to the irreducible representation

(a) A_g and B_g (b) A_g and A_u (c) A_u and B_g (d) B_g and B_u

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ANSWER KEY

1 (b)
2. (a)
3. (a)
4. (a)
5. (b)
6. (c)
7. (d)
8. (a)
9. (b)
10. (b)
11. (b)
12. (a)
13. (a)

Hints and Solutions

1.

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1
$\Gamma_{RR(3N)}$	9	–1	3	1

$$n_{A_1} = \frac{1}{4}[9-1+3+1] = 3$$

$$n_{A_2} = \frac{1}{4}[9-1-3-1] = 1$$

$$n_{B_1} = \frac{1}{4}[9+1+3-1] = 3$$

$$n_{B_2} = \frac{1}{4}[9+1-3+1] = 2$$

Total = $3A_1 + A_2 + 3B_1 + 2B_2$

2.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0
Γ_{RR}	12	0	2

$A_1 = \frac{1}{6}[12 + 0 + 6] = 3$

$A_2 = \frac{1}{6}[12 + 0 - 6] = 3$

$E = \frac{1}{6}[12 \times 2 \times 1 + 0 + 0] = 4$

$\Rightarrow \Gamma = 3A_1 + A_2 + 4E$

3.

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0
Γ_{RR}	6	3	0

$A_1 = \frac{1}{6}[1 \times 1 \times 6 + 3 \times 2 \times 1 + 0] =$

$A_2 = \frac{1}{6}[6 + 6 + 0] = 2$

$E = \frac{1}{6}[6 \times 2 \times 1 + 3 \times (-1) \times 2 + 0] = 1$

$\Rightarrow \Gamma = 2A_1 + 2A_2 + E$

4.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1
Γ				

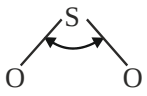
$A_1 = \frac{1}{4}[4 + 2 + 0 + 2] = \frac{8}{4} = 2$

$$A_2 = \frac{1}{4}[4 \times 1 \times 1 + 2 \times 1 \times 1 + 0 + 2 \times (-1) \times 1] = 1$$

$$B_1 = \frac{1}{4}[4 \times 1 \times 1 + 2 \times (-1) \times 1 + 0 + 2(-1) \times 1] = 0$$

$$B_2 = \frac{1}{4}[4 \times 1 \times 1 + 2 \times (-1) \times 1 + 0 + 2 \times 1 \times 1] = 1$$

$$\Rightarrow \Gamma = 2A_1 + A_2 + B_2$$

5. 

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1

6. In a character table the third column represent or give information about the translational or rotational active modes.

7. The direct product of two energy state should transform according to x, y or z axis for electronic transition.

   $a_1 \times a_1 = a_1$ = transition with z axis = allowed

   $a_1 \times e = e$ = transition with x, y axis = allowed

   $a_2 \times e = e$ = transition with x, y axis = allowed

   $a_1 \times a_2 = a_2$ = Not transition x, y or z = forbidden

   Correct answer is (d)

8. This irreducible representation is symmetric with respect to principal axis hence (A), also symmetric wrt subsiduary air (C_2') then Mulliken symbols is A_1.

9. Since the irreducible representation is 2 – D. the symbol starts with E_1 and Asymmetric w.r.t susiduary exis, has no value in σ_v (vertical mirror), but symmetric wrt to σ_h, hence E_2'.

10. Trace elements are the number of unshifted atom after apply certain operation.

    E : 4

    C_3 : 1

    σ_v : 2

11. A class is defined as the set of elements, which are conjugate to the another.

12. The Γ is symmetric wrt principal axis hence A and unsymmetric wrt subsidiary axis, Hence, A_2 muliken symbol.

13. $C_{2h} \rightarrow$ Point group $C_{2h} \rightarrow A_g, B_g, A_u + B_u$.

    Since C_{2h} Point group contains inversion centre (i), Therfore according to mutual exclusion principle, IR active modes are Raman inactive and Raman Active modes are IR inactive and mullikem symbols having (Ag, Bg) g in subscript are Raman active and that with subscript is (A_u, B_u) are IR active.

    $\therefore$ in trans–1, 3–butadiene having C_{2h} point group, the IRR's which are Raman active are A_g and B_g.

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DPP-12 GROUP THEORY

1. Which of the following mode is only Raman active in H_2O molecule?

(a) A_1 (b) B_1 (c) A_2 (d) None of these

2. The number of IR-active C – O stretching modes in cis[$Fe(CO)_4Cl_2$] molecule, which

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ	4	0	2	2

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	translational rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_x	yz

(a) $2A_1 + B_1 + B_2$, all four IR active (b) $2A_1 + B_1 + 2B_2$, all four IR active

(c) $2A_1 + B_1 + B_2$, but B_1 is IR active (d) $2A_1 + B_1 + B_2$, all IR active

3. Character table of C_{2v} point group is:

C_{2v}	E	C_2	σ_1	σ_2	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	–
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y

If the initial and final states belong to A_1 and B_1 irreducible representations respectively, the allowed electronic transition from A_1 to B_1 is:

(a) z-polarized (b) y-polarized (c) x-polarized (d) x, z-polarized

4. The transition that is allowed by x-polarized light in trans-butadiend is: (The character table for C_{2h} is given below).

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	R_x, x^2, y^2, z^3, xy
B_g	1	–1	1	–1	R_x, R_y, xz, yz
A_u	1	1	–1	–1	z
B_u	1	–1	–1	1	x, y

(a) $A_u \rightarrow A_g$ (b) $A_u \rightarrow B_g$ (c) $B_u \rightarrow B_g$ (d) $B_g \rightarrow A_g$

5. The E ⊗ E direct product in D_3 point group contains the irreducible representations

D_3	E	$2C_3$	$3C_2$
A_1	1	1	–1
A_2	1	1	–1
E_2	2	–1	0

(a) $A_2 + A_2 + E$ (b) $2A_1 + E$ (c) $2A_2 + E$ (d) $2A_1 + 2A_2$

6. Which statement is correct regarding C – O stretching modes for fac $[Mo(CO)_3(NCH_3)_3]$?

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	3	0	1

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, + z^2$
A_2	1	1	–1	R_z	$(x^2 – y2, xy)$
E	2	–1	0	(x, y) (R_x, R_y)	(xz, yz)

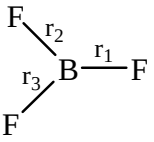
I. For this $\Gamma = A_1 + E$ II. A_1; symmetric stretching and IR active

III. E; IR active IV. A_1 and E both IR active but degenerate.

(a) I and II are correct (b) I and III are correct

(c) I, II and III are correct (d) I, II, III and IV are correct

7. In BF_3 molecule; r_1, r_2, r_3 are the three vectors correspond to each B–F bond, as shown below,



these belongs to which of the following reducible representation according to bond vector basis set.

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_1	3	1	1	3	1	1
Γ_2	3	0	1	3	0	1
Γ_3	4	1	2	4	1	2
Γ_4	4	0	1	4	0	1

(a) Γ_1 (b) Γ_2 (c) Γ_3 (d) Γ_4

8. Identify the symmetry species of the orbital $\psi = \psi_A - \psi_B$ in a C_{2v} NO_2 molecule, where ψ_A is an $O2p_x$ orbital on one O atom and ψ_B that on the other O atom.

(a) A_2 (b) A_1 (c) B_1 (d) B_2

9. Consider the C_{3v} ion NO_3^-. The orbital of the central N atom that can have a nonzero overlap with the combination $2p_z(A) - p_z(B) - p_z(C)$ of the three O atoms (with z perpendicular to the plane) are ?

(a) p_x (b) p_y (c) p_z (d) both p_x and p_y

10. The ClO_2 molecule (which belongs to the group C_{2v}) was trapped in a solid. Its ground state is known to be B_1. Light polarized parallel to the y-axis (parallel to the OO separation) excited the molecule to an upper state. What is the symmetry of that state?

(a) A_1 (b) A_2 (c) B_1 (d) B_2

11. What states of anthracene, may be reached by electric dipole transitions from their (totally symmetrical) ground states?

(a) A_{1g} (b) B_{3u} (c) A_{2u} (d) B_{1g}

12. The character table of the C_{2v} point group is given below:

C_{2v}	E	C_2	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1

The two functions $\varphi_1 = p_1 + 2p_2 + 2p_3 + p_4$ and $\varphi_2 = p_1 - p_2 - p_3 + 2p_4$ (where p_k is the p-orbital on the kth atom of cis-butadiene and σ_v is the molecular plane) belong to:

(a) A_1 and A_2 respectively (b) Both A_2

(c) Both B_2 (d) B_1 and B_2 respectively.

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ANSWER KEY

1 (c)
2. (a)
3. (c)
4. (b)
5. (a)
6. (c)
7. (d)
8. (a)
9. (d)
10. (b)
11. (b)
12. (c)

Hints and Solutions

1. A_2 mode of water molecule is only Raman active vibrational mode.

2.

	E	C_{2z}	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y
Γ	4	0	2	2	

$A_1 = \frac{1}{4}[4 + 0 + 2 + 2] = 2$

$B_1 = \frac{1}{4}[4 + 0 + 2 - 2] = 1$

$A_2 = \frac{1}{4}[4 + 0 - 2 - 2] = 0$

$B_2 = \frac{1}{4}[4 + 0 - 2 + 2] = 1$

$\Gamma = 2A_1 + B_1 + B_2$, all A_1, B_1, B_2 transformed according to z, x and y and hence IR active.

3. Transition A_1 to B_1 can be evaluated by direct product $A_1 \times B_1$ and its transformation.

	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	
	X	X	X	X	
B_1	1	-1	1	-1	
$A_1 \times B_1$	1	-1	1	-1	$= B_1$

B_1 transforms according to x-axis hence transition will be x-axis polarized.

4.

	E	C_2	σ_v	σ_v'	
A_u	1	1	–1	–1	
	X	X	X	X	
B_g	1	-1	1	-1	
$A_u \times B_g$	1	-1	–1	1	$= B_u$

B_u transforms according to x-axis hence transition will be x-axis polarized.

5. $E \times E = 2 \times 2 \quad (-1)(-1) \quad 0 \times 0$

$= 4 \quad 1 \quad 0$

$$n_{A_1} = \frac{1}{6}[4+2+0] = 1 \Rightarrow n_{A_2} = \frac{1}{6}[4+2-0] = 1 \Rightarrow n_E = \frac{1}{6}[8-2-10] = 1$$

Therefore, $E \times E = A_1 + A_2 + E$

Correct answer is (a)

6. $nA_1 = 1/6(3 \times 1 \times 1 + 0 + 1 \times 1 \times 3) = 1$

$nA_2 = 1/6(3 \times 1 \times 1 + 0 + 1 \times -1 \times 3) = 0$

$nE = 1/6(3 \times 2 \times 1 + 0 + 1 \times 0 \times 3) = 1$

For this $\Gamma = A_1 + E$

A_1 and E both are IR active. But, only E is degenerate.

7. For E all three vectors remain unchanged. Hence, it contribute 3.

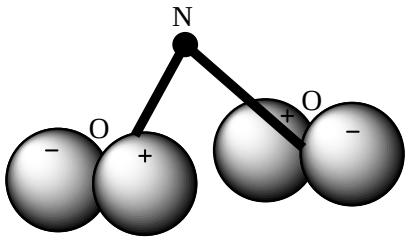
For C_3 all three bond vectors shifted. Hence, it contribute 0.

From these two values it is matched with Γ_2.

8. The negative sign in ψ indicates that the sign of ψ_B is opposite to that of ψ_A. We need to consider how the combination changes under each operation of the group, and then write the character as +1, –1, or 0 as specified above. Then we compare the resulting characters with each row in the character table for the point group, and hence identify the symmetry species.

The combination is shown in figure given below. Under C_2, ψ changes into itself, implying a

character of +1. Under the reflection σ_v, both orbitals change sign, so $\psi \rightarrow \psi$, implying a character of –1. Under σ_v', $\psi \rightarrow \psi$, so the character for this operation is also –1. The characters are therefore



$\chi(E) = 1 \qquad \psi(C_2) = 1 \qquad \chi(\sigma_v) = -1 \qquad \chi(\sigma_v') = -1$

These values match the characters of the A_2 symmetry species, so ψ can contribute to an a_2 orbital.

9. In order to have nonzero overlap with a combination of orbitals that spans E, an orbital on the central atom must itself have some E character, for only E can multiply E to give an overlap integral with a totally symmetric part. A galance at the character table shows that p_x and p_y orbitals available to a bonding N atom have the proper symmetry.

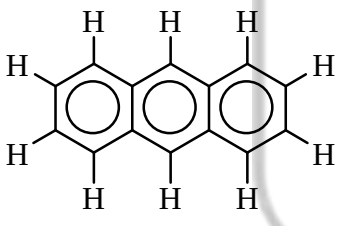
10. The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must be contain A_1. Then, since $\Gamma_i = B_1$, $\Gamma(\mu) = \Gamma(y) = B_2$ (C_{2v} character table), we candraw up the following table of characters

	E	C_2	σ_v	σ_v'
B_1	1	–1	–1	1
B_2	1	–1	1	–1
B_1B_2	1	1	–1	–1

$= A_2$

Hence, the upper state is A_2.

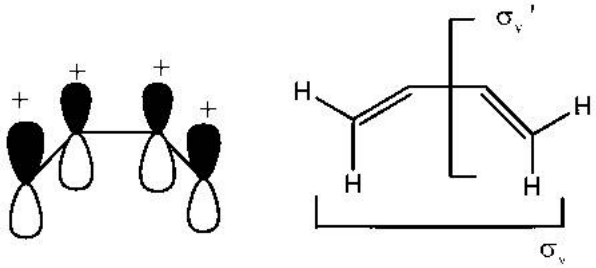
11. Anthracene



D_{2h}

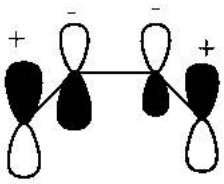
The components of μ span $B_{3u}(x)$, $B_{2u}(y)$, and $B_{tu}(z)$. The totally symmetric ground state in A_g. Since $A_g \times \Gamma = \Gamma$ in this group, the accessible upper terms are B_{3u} (x-polarized), B_{2u} (y-polarized), and B_{1u} (z-polarized).

12. $\psi_1 = P_1 + 2P_2 + 2P_3 + P_4$



	E	C_2	σ_v	σ_v'	
	1	-1	-1	1	$= B_2$,

$$\psi_2 = 2P_1 - P_2 - P_3 + 2P_4$$



	E	C_2	σ_v	σ_v'	
	1	-1	-1	1	$= B_2$

Both the molecular orbitals belongs to B_2.

Correct answer is (c).

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DPP-13 GROUP THEORY

1. The orbital $\psi = 1s_{HA} + 1S_{HB}$ of water belongs to the irreducible representation.

   (a) A_2 (b) B_2 (c) A_1 (d) B_1

2. Character table of C_{4v} point group is given below, the integrals $< d_{xy} \mid z \mid d_{x^2-y^2} >$, were transformed according to the representation

C_{4v}	E	$2C_{4z}$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2+y^2+z^2$
A_2	1	1	1	–1	1	R_z	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	–1	1	xy
E	2	0	–2	0	0	(x, y) (R_xR_y)	(xz, yz)

   (a) A_1 (b) B_1 (c) A_2 (d) B_2

3. Character table of C_{4v} point group is given below, the integral $< d_{xy} \mid l_z \mid d_{x^2-y^2} >$, is transformed according to the representation.

C_{4v}	E	$2C_{4z}$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2+y^2+z^2$
A_2	1	1	1	–1	1	R_z	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	–1	1	xy
E	2	0	–2	0	0	(x, y) (R_xR_y)	(xz, yz)

   (a) A_1 (b) A_2 (c) B_1 (d) B_2

4. Correct statement among the following are

   I. Molecule belonging to the point group T_h and T_d cannot be chiral.

II. The function xy has the symmetry species B_1 in the group C_{2v}.

III. A character X, is the sum of the diagonal elements as matrix representative.

(a) I, II (b) II, III (c) I, III (d) All are correct

5. Considering, z-axis as the rotational axis and, σ_{yz}-plane as the molecular plane, P_y orbital correspond to S atom of SO_2 belong to which of the following irreducible representation.

(a) A_1 (b) A_2 (c) B_1 (d) B_2

6. In XeF_4 molecule, having D_{4h} point group, where the z-axis is co-incident with the C_4-axis, the translational vector T_z, only placed on Xe-atom, belongs to the irreducible representation, character table of D_{4h} is

(a) A_{1u} (b) A_{2u} (c) B_{2u} (d) A_{2g}

7. CO_2 has

(a) 3 vibrational modes

(b) 4 vibrational modes, 2 of which are degenerate

(c) Stretching modes only

(b) An IR active symmetric stretch

8. Which of the following statement is correct:

(a) The symmetric stretching mode of PCl_3 is IR active and Raman inactive.

(b) The symmetric stretching mode of PCl_3 is IR active and Raman active.

(c) The symmetric stretching mode of PCl_3 is IR inactive and Raman active.

(b) The symmetric stretching mode of PCl_3 is IR inactive and Raman inactive.

9. The symmetric stretching mode of the SiF_4 molecule:

(a) Is IR active

(b) Is IR inactive.

(c) Generates a change in molecular dipole moment.

(d) Gives rise to a strong absorption in the IR spectrum.

10. An O_h XY_6 molecule exhibits two T_{lu} IR active modes. Which statement is true:

(a) Each T_{1u} mode is triply degenerate, and each give rise to one absorption in the IR spectrum XY_6.

(b) Each T_{1u} mode is triply degenerate, and each give rise to three absorption in the IR spectrum XY_6.

(c) Each T_{1u} mode is triply degenerate, and each give rise to three absorption in the IR spectrum XY_6.

(d) Each T_{1u} mode is the symmetric structure mode of XY_6.

11. The pair of symmetry points groups that are associated with only polar molecules is:

(a) C_{2v}, $D_{\infty h}$ (b) C_{2v}, C_{2h} (c) D_{2h}, T_d (d) C_{2v}, $C_{\infty h}$

12. The orbital $\psi = 1s_{H_A} - 1s_{H_B}$ of water belongs to the irreducible representation:

(a) A_1 (b) B_1 (c) A_2 (d) B_2

Use the character table below to answer Q. 13 and Q. 14 are

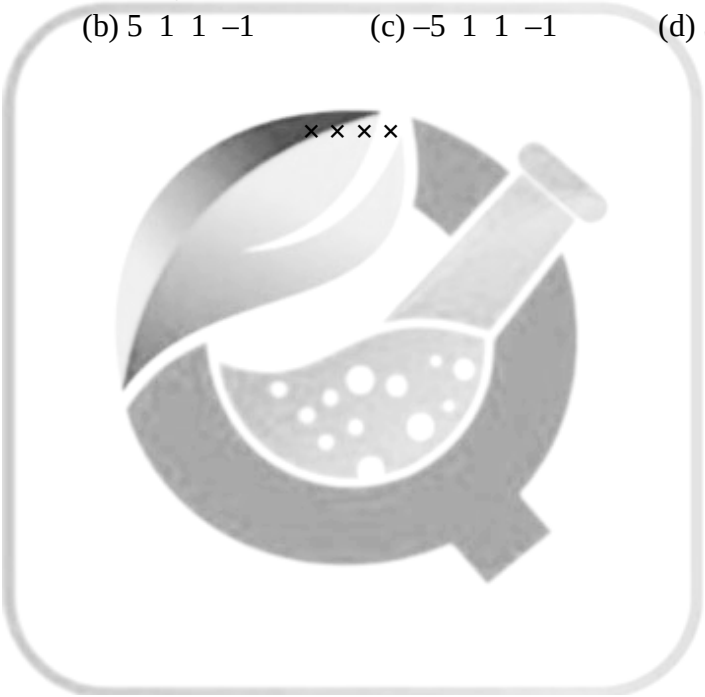
C_{2h}	E	C_2	i	σ_λ
Ag	1	1	1	1
Bg	1	–1	1	–1
Ae	1	1	–1	–1
Bu	1	–1	–1	1

13. What are the character of the reducible representation formed by its component irreducible representation $2B_u + A_g$

(a) 3 1 1 3 (b) –3 1 1 3 (c) 3 –1 –1 3 (d) 1 1 1 0

14. What are the character of the reducible representation formed by its component irreducible representation $B_g + A_u + 2B_u + A_g$

(a) 5 1 1 1 (b) 5 1 1 –1 (c) –5 1 1 –1 (d) 5 –1 –1 1



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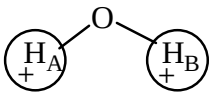
ANSWER KEY

1 (c)
2. (c)
3. (a)
4. (c)
5. (d)
6. (b)
7. (b)
8. (b)
9. (b)
10. (a)
11. (d)
12. (b)
13. (c)
14. (a)

Hints and Solutions

1. 

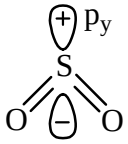
This is symmetric with respect to principle axis and vertical plane. Hence,

The orbital $\psi = Is_{H_A} + Is_{H_B}$ of water belongs to A_1 irreducible representation

2. In C_{4v} d_{xy}, $d_{x^2-y^2}$ spans B_2 and B_1 respectively, where Z-spans A_1, so
$< d_{xy} \mid z \mid d_{x^2-y^2} > = B_2 \times A_1 \times B_1 = B_2 \times B_1 = A_2$

3. d_{xy}, $d_{x^2-y^2}$ spans as B_2 and B_1 respectively and l_z transform as R_z which spans as A_2,
So, $< d_{xy} \mid l_z \mid d_{x^2-y^2} > = B_2 \times A_2 \times B_1 = B_2 \times B_2 = A_1$

4. Only statement II is incorrect, because xy function has the symmetry species A_2 in C_{2v} point group.

5. 

Assymertic w.r.t. principle axis and molecular plane. Hence, it belongs to B_2.

6.

D_{4h} ($4/mmm$)	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1		x^2-y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1		xy
E_g	2	0	–2	0	0	2	0	–2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z	
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1		
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1		
E_u	2	0	–2	0	0	–2	0	2	0	0	(x, y)	

Correct option is (b)

7. CO_2 has 4 degree vibration in which only 2 modes are IR active and which are degenerate.

8. PCl_3 is pyramidal in structure symmetric stretching of which result in IR activity and Raman activity.

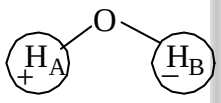
9. SiF_4 is tetrahedral in structure the symmetric stretching of tetrahedral is IR inactive

10. T represent the triply degenerate, 1, represent it is symmetric wrt principal axis and "u" suggest it is assymetric to inversion centre, hence they has only one absorption in the IR spectrum.

11. The polar point group are

$$C_{nv}, C_n, C_1, C_s, C_{\infty V}$$

Correct option is (d)

12. 

This is asymmetric with respect to principle axis and vertical plane. Hence,

The orbital $\psi = Is_{H_A} - Is_{H_B}$ of water belongs to B_1 irreducible representation

Correct option is (b)

13.

$2B_u$	2	–2	–2	2
A_g	1	1	1	1
	3	–1	–1	3

14.

B_g	1	–1	1	–1
A_u	1	1	–1	–1
$2B_u$	1	–2	–2	2
A_g	1	1	1	1
	5	–1	–1	1

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DPP-14 GROUP THEORY

1. What is the point group of "P_x" orbital

   (a) $C_{\infty v}$ (b) $D_{\infty h}$ (c) $D_{\infty d}$ (d) D_{∞}

2. What is point group of d_{xy} orbital

   (a) C_{2h} (b) C_{2v} (c) D_{2d} (d) D_{2h}

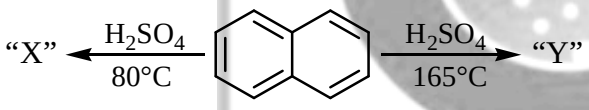
3. What is point group of dz^2 orbital

   (a) $D_{\infty h}$ (b) $D_{\infty Cl}$ (c) $D_{\infty n}$ (d) $D_{\infty v}$

4. Find the number of isomer of $C_2H_2Cl_2$ and determine the point group of the non polar one.

   (a) 3, C_{2v} (b) 2, C_{2h} (c) 4, C_{2v} (d) 3, C_{2h}

5. What is the point group of X and Y respectively in the following reaction

   (a) C_s and C_s respectively (b) C_{2h} and C_2 respectively

   (c) C_s and C_{2h} respectively (d) None of these

6. Which of the following is an example of abelian group,

   (I) 1, 1 dichloroethylene (II) 1, 2 dichloroethylene cis (III) Ammonia

   (a) I only (b) I and II only (c) II only (d) I, II, II

7. The symmetric stretching mode for PCl_3 is of A, symmetry. In the C_{3v} character table, there are z and ($x^2 + y^2$, z^2) entries in the A_1 row. This tells you that:

   (a) The symmetric stretching mode of PCl_3 is IR active and Raman inactive

   (b) The symmetric stretching mode of PCl_3 is IR active and Raman active

   (c) The symmetric stretching mode of PCl_3 is IR inactive and Raman active

   (d) The symmetric stretching mode of PCl_3 is IR active and Raman active

8. An octahedral XY_6 molecule exhibit term T_{1u} IR active mode which statement is true?

   (a) Each T_{1u} mode is triply degenerate and each give rise to one absorption in the IR spectrum of XY_6.

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Contact Us : 9990382567, 7082062392, 9717373074, 8285815185

(b) Each T_{1u} mode is triply degenerate and each give rise to three absorption in the IR spectrum of XY_6.

(c) Each T_{1u} mode is non-degenerate, give rise to one absorption in the spectrum of XY_6.

(d) One of the degenerate $T,_u$ mode is the symmetric stretch mode is XY_6.

9. The IR spectrum of XY_3 shows absorption at 480, 691 and 1449 cm^{-1}. Use these data to decide the point group of XY_3.

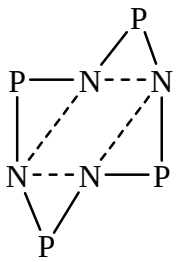
(a) C_{3v} (b) D_{3h} (c) Cannot predicted (d) None

10. The IR spectrum of gaseous XY_4 shows absorption at 55 and 254 cm^{-1}. Use the data to decide the point group of XY_4.

(a) D_{4h} (b) T_d (c) Cannot be predicted (d) None

11. Matrices which describes the transformation of set of coordinate by proper and improper rotation are called ____ matrices.

(a) orthogonal (b) conjugate (c) inverse (d) diagonal

12.  is of which point group?

(a) C_{2h} (b) C_{2v} (c) C_{2d} (d) D_{2h}

13. Which of the following satisfy the condition of abelian group?

(a) AB = BA (b) AB ≠ BA (c) AB + BA = 0 (d) $AB = A^{-1}B^{-1}$

14. Match the following

(A) Plane	(i) Inversion of all atom through the centre
(B) Centre of symmetry	(ii) One or more rotation about the axis
(C) Proper axis	(iii) Reflection
(D) Improper axis	(iv) One or more repetition of the sequence: rotation followed by reflection in a plane perpendicular to the rotation axis.

(a) A (iv) B (i) C (ii) D (iv) (b) A (ii) B (i) C (iii) D (iv)

(c) A (iii) B (i) C (ii) D (iv) (d) A (iii) B (ii) C (iv) D (i)

15. Which of the following statement is/are true?

(a) all assymmetric molecule are disymmetric (b) all dissymmetric molecule are assymetric

(c) Both (a) and (b) (d) Neither (a) nor (b)

× × × ×

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ANSWER KEY

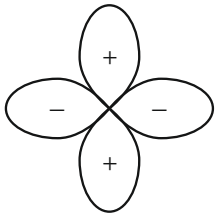
1 (d)
2. (d)
3. (a)
4. (d)
5. (a)
6. (b)
7. (d)
8. (a)
9. (b)
10. (b)
11. (a)
12. (a)
13. (a)
14. (c)
15. (a)

Hints and Solutions

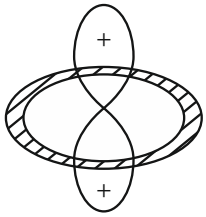
1. 

linear but no (i) is present
hence point gruop $C_{\infty v}$

Correct option is (d).

2. 

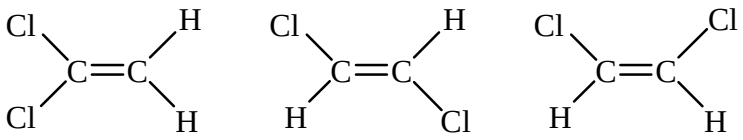
C_2 axis (P.A.)
2 perpendicular C_2' and σ_h
point group D_{2h}

3. 

linear with centre of symmetry
hence $D_{\infty h}$

Correct option (a).

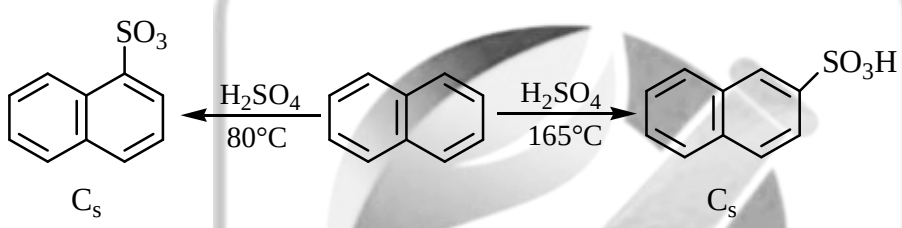
4. The distinct isomers are



Polar
Point group C_{2v}

Non-Polar
Point group C_{2h}

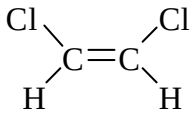
Polar
Point group C_{2v}

5. 

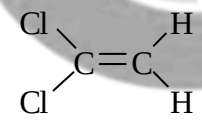
C_s
Only plane of symmetry

C_s
Only plane of symmetry

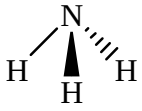
6. Any point group which do not posses axis of symmetry greater than two fold is known as abelian group



C_{2h} : only C_2



C_{2v} (only C_2)



: C_{3v} contain C_3

7. If the symmetry label (A, B, E) of a normal mode of vibration is associated with x, y or z in the character table then the mode is IR active.

   If the symmetry label (A, B, E etc.) of a normal mode of vibration is associated with x^2, xy, yz, $x^2 - y^2$, $x^2 + y^2$, z^2) in the character table, then mode is raman active.

8. T represent the triply degenerate, 1, represent it is symmetric wrt principal axis and "u" suggest it is assymetric to inversion centre, hence they has only one absorption in the IR spectrum.

9. XY_3 contains 6 degree of vibration, but in D_{3h} only 3 are IR active and in C_{3v} all 6 are IR active hence point group of XY_3 here is D_{3h}.

10. XY_4 contains a degree of vibration but in D_{4h} only 3 are IR active and in T_d only 2 are IR active. So, point group of XY_4 is "T_d".

11. Orthogonal matrices are defined as the matrices which describes the transformation of set of coordinate by proper and improper rotation

12. The given molecule contains C_2 axis and plane perpendicular to it

So the point group is C_{2h}

13. The groups in which combination is commutative are caused the abelian group.

$\Rightarrow$ AB = BA (commutative property)

14. The symmetry operation of the following are as follows:

Symmetry Element	Symmetry Operation
Plane	Reflection
Centre of symmetry	Inverting the coordinates
Proper axis	Rotation
Improper axis	Rotation followed by reflection

15. The molecule that are not superimposable on their mirror images are termed dissymmetric. This term is used rather than assymetric,since the latter means, literally, have no symmetry; that is, it is applicable only to a molecule belonging to point group C_1. All asymmetric molecules possess some symmetry, but the converse is not true.

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